

## THE ROLE OF CATALYST PRECURSOR ANIONS IN CHAR REACTIVITY

Lillian L. Sims, Godfried M. K. Abotsi and Kofi B. Bota

Research Center for Science and Technology

Clark Atlanta University

Atlanta, GA 30314

**Key words:** Anions, zeta potential, metal adsorption

### INTRODUCTION

Coal gasification activity is generally attributed to the metal components of catalyst precursors. However, there is evidence that the anion of the catalytic salt plays a significant role in the performance of the catalyst. It has been reported (1) that for the same metal, the chlorides, acetates, or hydroxides of sodium, potassium, magnesium, and calcium exhibited different char reactivities. The catalysts were loaded from aqueous solution. For example, at 1223K, the order of reactivity for the sodium compounds was  $\text{NaOH} > \text{NaAc} > \text{NaCl}$ . These findings were rationalized in terms of the influence of the various anions on the diffusivities of the cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  produced by dissociation of the metal precursors at gasification temperatures) through the pores of the chars. The variations in the activities of the catalysts were also ascribed to differences in the extent of deactivation as a result of the catalyst reaction with inorganic materials in the coal, and to the presence or absence of coal surface metal-oxygen complexes which have been hypothesized as prerequisites for coal char reactivity (2-7). It has also been suggested that the metal ion of the catalyst salt reacts with the carbon in the char to form active intermediates for gasification and that the anion of the salt favorably modifies the structure of the active species. However, the composition and structure of the active intermediates are unknown (8).

Since coal is normally impregnated with catalyst from solution, the variations in the activities of different catalyst precursors may be due to the influence of different anions during the adsorption of the metal ions onto the coal. The surface charge properties of aqueous suspensions of coal is well known. The electrical potential on a coal particle decreases rapidly with distance from the charged coal surface. The effective thickness is the distance from the charged surface into the solution within which most of the electrical interactions with the surface occur (9,10). The effective thickness,  $1/K$ , (or the Debye length) is given by the expression (9,10):

$$1/K = \left[ \frac{(\epsilon_r RT)}{(4\pi F^2 \sum_i C_i Z_i^2)} \right]^{1/2} \quad (1)$$

where  $\epsilon_r = \epsilon/\epsilon_0$  = the relative static permittivity or dielectric constant of the solution ( $\epsilon$  = the static permittivity of the solution and  $\epsilon_0$  = the permittivity of a vacuum),  $R$  = the gas constant,  $T$  = the absolute temperature,  $F$  = the Faraday constant,  $C_i$  = the molar concentration of any ion in solution. The above equation shows that  $1/K$  is inversely proportional to both the valence ( $Z$ ) of the ions in solution and to the square root of their ionic concentrations. Also, in the presence of an electrolyte, the electrical effects are experienced over shorter distances (due to the compression of the electrical double layer) than in the absence of an electrolyte. Thus, the Debye length decreases rapidly with increasing ionic strength, given by  $1/2\sum C_i Z_i^2$  (10).

In relation to catalyzed coal gasification, it is apparent from the above discussion that when different catalyst precursor electrolytes containing the same metal (e.g. KCl and  $K_2CO_3$ ) are dissolved in aqueous solution and separately introduced into coal, the degree of coal-metal ion contact will be different for the various catalyst precursors due to differences in the double layer thickness. This will produce different metal adsorption densities and possibly different catalyst dispersion and gasification activities. Variations in catalyst uptake by coals can also occur as a result of differences in the pHs of the impregnating metal solutions. This work reports on the effects of catalyst precursor anions and pH on coal electrokinetic properties and catalyst adsorption by various calcium and potassium catalyst precursors.

## EXPERIMENTAL

The surface electrokinetic properties of the raw coal (North Dakota Hagel lignite, PSOC 1482) in the presence or absence of acetate ( $CH_3COO^-$ ), chloride ( $Cl^-$ ), nitrate ( $NO_3^-$ ), carbonate ( $CO_3^{2-}$ ) or sulfate ( $SO_4^{2-}$ ) anion was investigated by dispersing 300 mg of the coal (-200 mesh sieve size) in a liter of distilled water containing  $10^{-1}$ ,  $10^{-2}$  or  $10^{-3}$  mol/L of each anion. The potassium compound of each anion was used as the source of the anion while the acetate, chloride or nitrate of calcium was applied. The slurries were divided into 50.0 mL portions and the pHs were adjusted with a few drops of dilute nitric acid or ammonium hydroxide solution. The slurries were mechanically agitated for 3h to attain equilibrium followed by determination of the pHs and the zeta potentials using "Pen Kem model 501 Lazer Zee Meter."

The effects of the surface charge properties of the coal on the adsorption of potassium from  $CH_3COOK$ , KCl,  $KNO_3$ ,  $K_2CO_3$  or  $K_2SO_4$  solution has been ascertained by agitation (for 24h) of 4.0 g of the coal with 100 mL of solution containing  $10^{-1}$  mol/L potassium metal. The catalyst precursors were used separately. Following the adsorptions, the coal particles were filtered and the potassium content in the coal samples was determined by Galbraith Laboratories, Inc.

## RESULTS AND DISCUSSION

The effects of chloride anion concentration on the zeta potentials of the coal particles are shown in Figures 1 and 2, respectively, for  $CaCl_2$  and KCl catalyst precursors. As can be observed from Figure 1, the charge density on the coal particles becomes progressively more negative, in the absence of added chloride anions, as the pH

of the slurry was raised from acidic to basic. However, addition of  $10^{-2}$  or  $10^{-3}$  mol/L chloride anion significantly reduced the net negative surface charge on the coal particles, especially at the higher chloride anion concentration. At  $\sim$  pH 10, for instance, the zeta potential of the coal is about -78 mV in the absence of chloride anion, but decreased to -15 and -40 mV, for the  $10^{-2}$  and  $10^{-3}$  mol/L  $\text{Cl}^-$  concentrations, respectively. Since the original coal particles are negatively charged, chloride anion adsorption will be hindered as a result of electrostatic repulsion between the coal surface and the chloride anion. Thus, the reduction in surface charge density must arise from the adsorption of calcium ions produced from the dissociation of calcium chloride, the driving force for the adsorption being coulombic attraction between the anionic coal surface and the calcium cations.

As in the case of the  $\text{CaCl}_2$  precursor, Figure 2 shows that the zeta potentials of the coal particles decrease with increase in pH when KCl is used as the  $\text{Cl}^-$  source. It is also observed that, within experimental error, addition of KCl produces a less negative zeta potential compared to that on the coal without KCl addition. The development of surface charge on coal particles in aqueous media has been attributed to the dissociation of coal surface carboxylic and hydroxyl groups as discussed by several investigators (9,11-13). Comparison of Figures 1 and 2 shows that the reduction in the negative zeta potentials is more prominent, at similar chloride concentrations, for  $\text{CaCl}_2$  than KCl. This behavior is consistent with equation (1) which predicts that the Debye length should be shorter in the presence of  $\text{CaCl}_2$  than for KCl due to the higher ionic charge on  $\text{Ca}^{2+}$  compared to that on  $\text{K}^+$ . This compression of the double layer promotes higher  $\text{Ca}^{2+}$  than  $\text{K}^+$  uptake and results in a greater reduction in the net negative surface charge density in the presence of  $\text{CaCl}_2$ . Similar trends were observed for the other corresponding calcium and potassium salts. To maintain a constant double layer thickness in studies involving interfacial phenomena, an excess of a 1:1 supporting electrolyte is normally added to the system. However, a supporting electrolyte was not applied in the current study in order to determine the influence of the various catalyst precursor anions or cations on coal surface chemistry.

The dependence of zeta potentials on pH and carbonate anion concentration, when using  $\text{K}_2\text{CO}_3$  as  $\text{CO}_3^{2-}$  source, is provided in Figure 3. Similar zeta potentials were obtained in the presence or absence of  $\text{CO}_3^{2-}$ , particularly around  $\sim$  pH 2 - 4.5, for the  $10^{-2}$  or  $10^{-3}$  mol/L  $\text{CO}_3^{2-}$  concentration. However, significant reductions in the negative zeta potentials occurred at  $10^{-1}$  mol/L  $\text{CO}_3^{2-}$ . The influence of the surface electrical properties of the coal on potassium adsorption from aqueous solutions of the potassium compounds is presented in Figure 4. The potassium uptake shows two distinct features: (1) a strong dependence on coal slurry pH, and (2) a dependence on the potassium salt used. For all the compounds, potassium adsorption was minimum around pH 2, it was maximum at  $\sim$  pH 10 and intermediate at pHs between 5 and 6. From Figure 4, it appears that at a given pH, the metal uptake can be classified into three groups according to the potassium precursor used: KCl,  $\text{KNO}_3$  and  $\text{K}_2\text{SO}_4$  fall into one group, while  $\text{KOOCCH}_3$  and  $\text{K}_2\text{CO}_3$  belong to separate groups. It is evident from Figure 4 that the highest potassium loading was obtained at all pHs when adsorption was effected using potassium carbonate solution. The second highest metal uptake occurred when potassium acetate was used and approximately the same level of potassium was adsorbed from potassium chloride, potassium nitrate and potassium acetate solutions. As can be seen from Figure 3, the net negative surface charge density on the coal is significantly reduced in  $10^{-1}$  mol/L  $\text{CO}_3^{2-}$  solution when  $\text{K}_2\text{CO}_3$  was used as the carbonate anion precursor. The observed potassium loadings from this salt is in agreement with the zeta potential results. Thus, the surface charge on the coal clearly plays a role in potassium uptake. However,

the reasons for the variations in metal adsorption as a function of anion type are not known at this time and are the subjects of continuing research.

In conclusion, it has been shown that the negative charge density on a North Dakota lignite is reduced in the presence of  $\text{CH}_3\text{COOK}$ ,  $\text{KCl}$ ,  $\text{KNO}_3$ ,  $\text{K}_2\text{CO}_3$  or  $\text{K}_2\text{SO}_4$  solutions. For each compound, the reduction becomes more prominent as the salt concentration is increased, the phenomenon being particularly distinct for  $\text{K}_2\text{CO}_3$ . Adsorption studies show that the highest potassium adsorption occurs from aqueous  $\text{K}_2\text{CO}_3$  solution, thus confirming the zeta potential results which were least negative at  $10^{-1}$  mol/L  $\text{CO}_3^{2-}$  when using  $\text{K}_2\text{CO}_3$  salt. The reported superior activity of  $\text{K}_2\text{CO}_3$  in char reactivity may reside in its stronger interaction with the coal surface during catalyst loading from solution. Fourier transform infrared studies are also in progress to gain insight into the interaction between the coal surface and the various ions.

#### ACKNOWLEDGEMENT

Financial support for this research was provided by the U. S. Department of Energy under contract number DE-FG22-91PC91286.

#### REFERENCES

1. Calahorra, C. V.; Gonzalez, C. F.; Garcia, A. B.; Serrano, V. G., *Fuel* 1987, 66, 216.
2. Wigmans, T.; Haringa, H.; Moulijn, J. A., *Fuel* 1983, 62, 185.
3. Hashimoto, K.; Miura, K.; Xu, J. J.; Watanabe, A.; Masukami, H. *Fuel* 1986, 65, 489.
4. Wigmans, T.; van Craneburgh, H.; Elfring, R.; Moulijn, J. A., *Carbon* 1983, 21, 23.
5. Yuh, S. J.; Wolf, E. E., *Fuel* 1983, 62, 252.
6. Fredriks, I. L. C.; van Wechem, H. M. H.; Stuiver, J. C. M.; Bouwman, R., *Fuel* 1981, 60, 463.
7. Mims, C. A.; Rose, K. D.; Melchior, M.-T.; Pabst, J. K., *J. Am. Chem. Soc.*, 1982, 104, 6886.
8. Wood, B. J. and Sancier, K. M. *Catal. Rev. Sci. Eng.* 1984, 26(2), 233.
9. Laskowski, J. S., Parfitt, G. D., In "Interfacial Phenomena in Coal Technology," Botsaris, G. D. and Glazman, Y. M., Eds., Marcel Dekker, New York, 1988, p. 279.
10. Rosen, M. J., "Surfactants and Interfacial Phenomena," John Wiley, New York, 1978, p. 31.

11. Kelebek, S., Salman, T.; Smith, G. W., *Canad. Metal. Quart.* 1982, 21, 205.
12. Abotsi, G. M. K., Bota, K. B., Saha, G., *Energy & Fuels* 1992, 6, 779.
13. Fuerstenau, D. W.; Rosenbaum, J. M.; Laskowski, J., S., *Coll. Surf.* 1983, 8, 137.

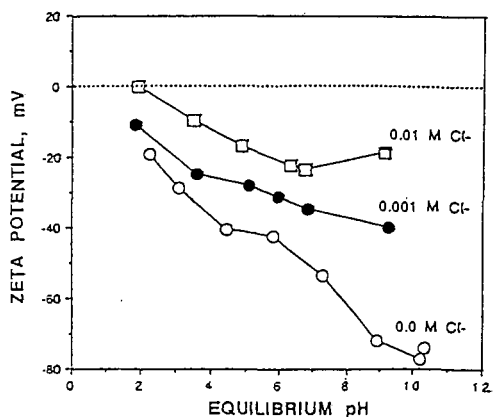


Figure 1. Dependence of zeta potential on the coal slurry pH and chloride anion concentration using  $\text{CaCl}_2$  as the source of chloride. Coal: North Dakota lignite.

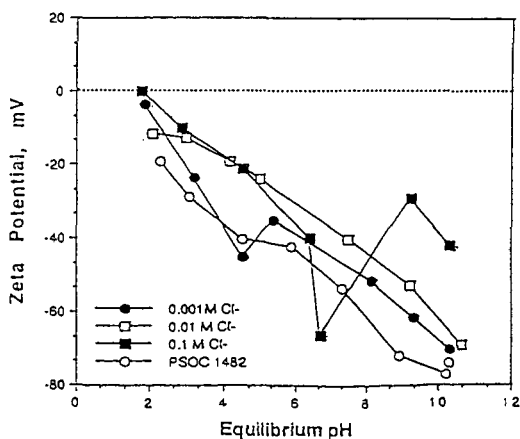


Figure 2. Dependence of the coal's zeta potential on pH and chloride anion concentration. KCl as source of chloride.

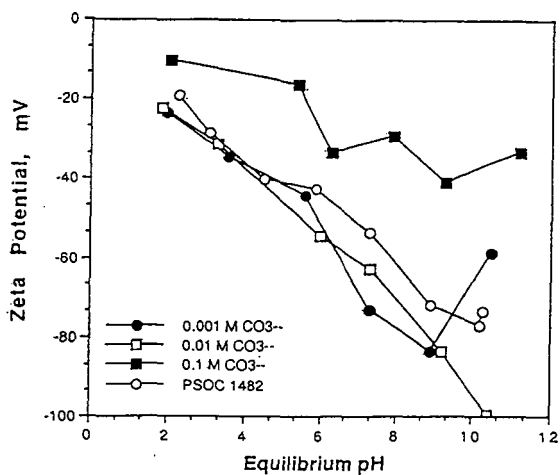


Figure 3. Variation of the coal's zeta potential with pH and carbonate anion concentration.  $K_2CO_3$  as source of carbonate anion.

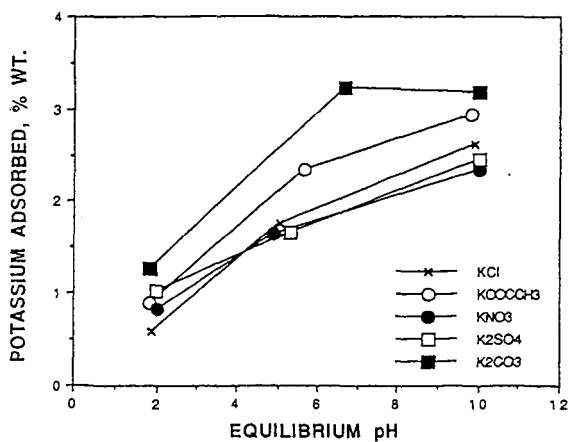


Figure 4. Influence of various potassium salts and pH on potassium adsorption by the coal.